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Inventors: **SANDOR NAGY, RAMESH KRISHNAMURTI, JOHN A. TYRELL, LEONARD V. CRIBBS, MARY COCOMAN, AND BRADLEY P. ETHERTON**

For: **TRANSITION METAL CATALYSTS CONTAINING BIDENTATE LIGANDS AND METHOD OF USING AND PREPARING SAME**

Enclosed are:

☐   A Declaration of the Inventors;

☐   Powers of Attorney by Inventors;

☐   An Assignment of the invention to Lyondell Petrochemical Company;

☐   Form PTO-1595 Recordation Cover Sheet;

☐   Information Disclosure Statement with Form PTO-1449 and cited references; and

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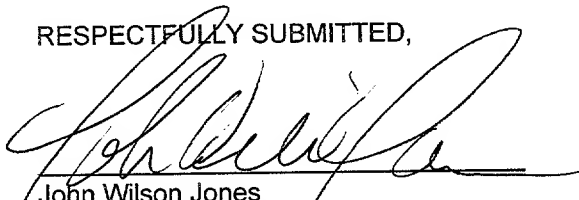| FOR	(Col. 1) NO. FILED	(Col. 2) NO. EXTRA
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Applicants:
    Sandor Nagy, et al.
 	
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For: TRANSITION METAL CATALYSTS
      CONTAINING BIDENTATE LIGANDS
      AND METHOD OF USING AND
      PREPARING SAME
	§ § § § § § § § § § §	Attorney Docket No. 016199/1110

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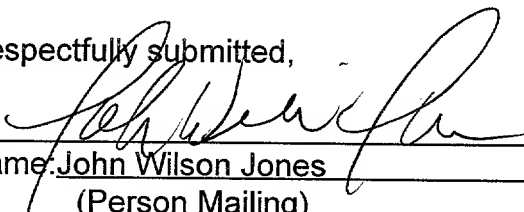 and Trademarks
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(1)   Patent application including specification, 20 claims and abstract (27 pages);

(2)   Fee sheet (in duplicate); and

(3)   Postcard.

Respectfully submitted,

Date: June 9, 1997

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TITLE: TRANSITION METAL CATALYSTS CONTAINING BIDENTATE LIGANDS AND METHOD OF USING AND PREPARING SAME

INVENTORS: SANDOR NAGY, RAMESH KRISHNAMURTI, JOHN A. TYRELL, LEONARD V. CRIBBS, MARY COCOMAN, AND BRADLEY P. ETHERTON

This is a continuation-in-part application of U.S. Patent Application Serial No. 08/423,232, filed April 17, 1995.

Background of the Invention

This invention relates to catalysts useful in polymerizing α-olefins. In particular, it relates to the polymerization of ethylene using transition metal catalysts with bidentate ligands containing pyridine or quinoline moieties.

Until recently, polyolefins have been made primarily using conventional Ziegler catalyst systems. A Ziegler catalyst typically consists of a transition metal-containing compound and one or more organometallic compounds. For example, polyethylene has been made using Ziegler catalysts such as titanium trichloride and diethylaluminum chloride, or a mixture of titanium tetrachloride, vanadium oxytrichloride, and triethylaluminum. These catalysts are inexpensive but they have low activity and therefore must be used at high concentrations. The catalyst residue in the polymers produce a yellow or grey color and poor ultraviolet and long term stability, and chloride-containing residues can cause corrosion in polymer processing equipment. It is therefore sometimes necessary to either remove catalyst residues from the polymer or add neutralizing agents and stabilizers to the

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polymer to overcome the deleterious effects of the residues and this adds to production costs. Furthermore, Ziegler catalysts produce polymers having a broad molecular weight distribution, which is undesirable for some applications such as injection molding. They are also poor at incorporating α-olefin co-monomers,

5   making it difficult to control polymer density. Large quantities of excess co-monomer may be required to achieve a certain density and many higher α-olefins, such as 1-octene, can be incorporated at only very low levels, if at all.

Although substantial improvements in Ziegler catalyst systems have occurred since their discovery, these catalysts are now being replaced with recently

10   discovered metallocene catalyst systems. A metallocene catalyst typically consists of a transition metal compound that has one or more cyclopentadienyl ring ligands. Metallocenes have low activities when used with organometallic compounds, such as aluminum alkyls, which are used with traditional Ziegler catalysts, but very high activities when used with aluminoxanes as cocatalysts. The activities are generally

15   so high that catalyst residues need not be removed from the polymer. Furthermore, they produce polymers with high molecular weights and narrow molecular weight distributions. They also incorporate α-olefin co-monomers well.

However, at higher temperatures metallocene catalysts tend to produce lower molecular weight polymers. Thus, they are useful for gas phase and slurry

20   polymerizations of ethylene, which are conducted at about 80°C to about 95°C, but in general they do not work well as temperatures are increased. The polymerization of ethylene in solution is desirable because it allows great flexibility for producing
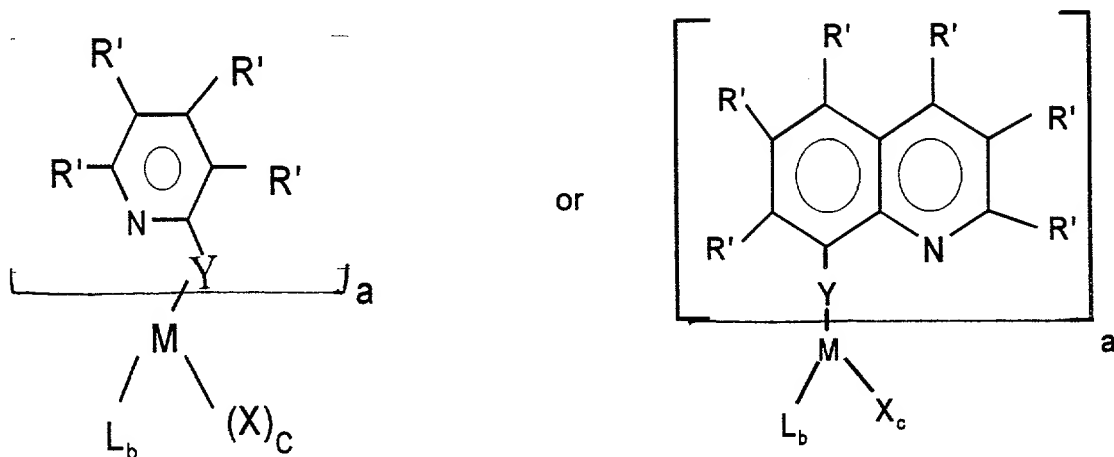
polymers over a wide range of molecular weights and densities as well as the use of a large variety of different co-monomers. Solution polymerization permits the production of polymers that are useful in many different applications. For example, both high molecular weight, high density polyethylene (PE) film useful as a barrier

5   film for food packaging and low density ethylene co-polymers with good toughness and high impact strength can be made.
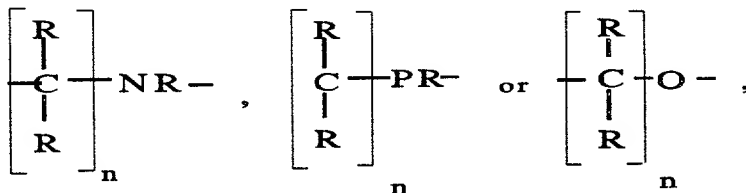
Summary of the Invention

    We have discovered novel bidentate pyridine transition metal compounds which have excellent activity as α-olefin polymerization catalysts. We have also

10   discovered that bidentate quinoline transition metal compounds, which were heretofore unsuspected of possessing any catalytic properties, are also excellent polymerization catalysts for α-olefins. These catalysts produce polymers having properties very close to the properties of polymers produced using metallocene catalysts. That is, the polymers have a narrow molecular weight distribution and a

15   uniform co-monomer incorporation.

Description of the Preferred Embodiments

The transition metal catalysts of this invention containing the bidentate

pyridine based ligand have the general formula


or

where Y is O, S, NR, PR,

$$\left[\begin{array}{c} R \\ | \\ C \\ | \\ R \end{array}\right]_n \!\!-NR-\;, \qquad \left[\begin{array}{c} R \\ | \\ C \\ | \\ R \end{array}\right]_n \!\!-PR- \quad \text{or} \quad -\left[\begin{array}{c} R \\ | \\ C \\ | \\ R \end{array}\right]_n \!\!-O-\;,$$

each R is independently selected from hydrogen, C_1 to C_6 alkyl, or C_6 to C_{14} aryl,

each R' is independently selected from R, C_1 to C_6 alkoxy, C_7 to C_{20} alkaryl, C_7 to C_{20}

aralkyl, halogen, or CF_3, M is a Group 3 to 10 metal, each X is independently

selected from halogen, C_1 to C_6 alkyl, C_6 to C_{14} aryl, C_7 to C_{20} alkaryl, C_7 to C_{20}

aralkyl, C_1 to C_6 alkoxy, or

$$-N\!\!\begin{array}{c} \diagup R \\ \diagdown R \end{array}\;,$$
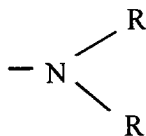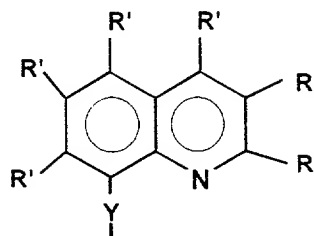
L is X, cyclopentadienyl, C_1 to C_6 alkyl substituted cyclopentadienyl, indenyl, fluorenyl, or

or

"n" is 1 to 4;

"a" is 1 to 3;

"b" is 0 to 2;

$a + b \leq 3$;

"c" is 1 to 6; and

a + b + c equals the oxidation state of M.

In the formula, the Y group is preferably oxygen as those compounds are easier to make. For the same reason the R group is preferably methyl and all of the R' are hydrogen. The L group is preferably halogen, most preferably chlorine, as those catalysts give superior properties and are easier to prepare. For the same reasons, the X group is preferably halogen, especially chlorine. The M group is preferably a Group 3 to 7 metal, most preferably a Group 4, 5 or 6 metal such as zirconium, hafnium or titanium.

In a preferred embodiment of the invention

$a + b \leq 2$ when the oxidation state of M is 4 or less; and

$a + b \leq 3$ when the oxidation state of M is greater than 4.

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With the latter, a + b most preferably is less than or equal to 2 when the oxidation state of M is greater than 4.

Preparation of the bidentate pyridine complexes is illustrated in the examples, but generally they can be prepared by reacting a substituted pyridine precursor having an acidic proton with a compound having the formula MX_3L in the presence of an HX scavenger. The reaction is stoichiometric and stoichiometric amounts of scavenger are preferred. Examples of suitable scavengers include compounds that are more basic than the substituted pyridine, such as triethylamine, pyridine, sodium hydride, and butyl lithium. If the scavenger is a stronger base than the substituted pyridine one can make a salt of the substituted pyridine and begin with that. While the reaction is preferably performed in a solvent, only partial solubility of the reactants is required. An aprotic solvent, such as tetrahydrofuran (THF), ether, toluene, or xylene, can be used at about 0.2 to about 20 wt% solids, and preferably at about 5 to about 10 wt% solids. The reaction can occur at about -78°C to about room temperature. As the reaction proceeds a precipitate is formed and the product can be extracted with toluene, methylene chloride, diethyl ether, or a similar extractant.

The bidentate quinoline transition metal catalysts of this invention have the general formula

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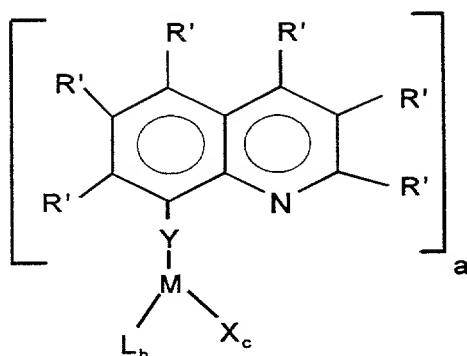
where R, R', L, M, X, "n", "a", "b" and "c" were as previously defined.

The quinoline transition metal catalysts are made in a similar manner to the pyridine transition metal catalysts except that one begins with a substituted quinoline such as 8-hydroxy quinoline (also known as 8-quinolinol) instead of the substituted pyridine. Also, butyl lithium can be used in a solvent to make the lithium salt of 8-hydroxy quinoline, which can also be used as the starting material.

The catalysts of the invention are normally used in combination with a co-catalyst. Such cocatalysts (or activators) are any compound or component which can activate the catalyst. Representative co-catalysts include alumoxanes and aluminum alkyls of the formula $Al(R_7)_3$ wherein R^7 independently denotes a C_1-C_8 alkyl group, hydrogen or halogen. Exemplary of the latter of such co-catalysts are triethylaluminum, trimethylaluminum and tri-isobutyl aluminum. The alumoxanes may be represented by the cyclic formulae $(R^{15}\text{-}Al\text{-}O)_g$ and the linear formula $R^{15}(R^{15}\text{-}Al\text{-}O)_s AlR^{15}$ wherein R^{15} is a C_1-C_5 alkyl group such as methyl, ethyl, propyl, butyl and pentyl, g is an integer from 1 to about 20 and s is about 2 to about 10. Preferably, R^{15} is methyl and g is about 4. Representative but non-exhaustive examples of alumoxane co-catalysts are (poly)methylalumoxane (MAO), ethylalumoxane and diisobutylalumoxane.

The mole ratio of such co-catalysts to catalyst when used in a polymerization is generally in the range 0.01:1 to 100,000:1, and preferably ranges from 1:1 to 10,000:1.

An alternative co-catalyst is an acid salt that contains a non-coordinating inert anion (see U.S. Patent No. 5,064,802). The acid salt is generally a non-nucleophilic compound that consists of bulky ligands attached to a boron or aluminum atom, such as lithium tetrakis(pentafluorophenyl) borate, lithium tetrakis(pentafluorophenyl)aluminate, anilinium tetrakis(pentafluorophenyl)borate, and mixtures thereof. The anion which results when these compounds react with the catalyst is believed to be weakly coordinated to the metal-containing cation. The mole ratio of acid salt to catalyst can range from about 0.01:1 to about 1000:1, but is preferably about 1:1 to 10:1. While there is no limitation on the method of preparing an active catalyst system from the catalyst and the acid salt, preferably they are mixed in an inert solvent at temperatures in the range of about -78°C to about 150°C. They can also be mixed in the presence of monomer if desired. The acid salt can be used in combination with the above referenced cocatalysts described earlier.

The catalyst and co-catalyst can be used on a support such as silica gel, alumina, silica, magnesia, or titania, but supports are not preferred as they may leave contaminants in the polymer. However, a support may be required depending

upon the process being utilized. For example, a support is generally needed in gas phase polymerization processes and slurry polymerization processes in order to control the particle size of the polymer being produced and in order to prevent fouling of the reactor walls. To use a support, the catalyst and co-catalyst are

5   dissolved in the solvent and are precipitated onto the support material by, for example, evaporating the solvent. The co-catalyst can also be deposited on the support or it can be introduced into the reactor separately from the supported catalyst.

The catalyst is used in a conventional manner in the polymerization of olefinic

10   hydrocarbon monomers. While unsaturated monomers such as styrene can be polymerized using the catalysts of this invention, it is particularly useful for polymerizing α-olefins such as propylene, 1-butene, 1-hexene, 1-octene, and especially ethylene.

The catalyst is also useful in a conventional manner for copolymerizing

15   mixtures of unsaturated monomers such as ethylene, propylene, 1-butene, 1-hexene, 1-octene, and the like; mixtures of ethylene and di-olefins such as 1,3-butadiene, 1,4-hexadiene, 1,5-hexadiene, and the like; and mixtures of ethylene and unsaturated comonomers such as norbornene, ethylidene norbornene, vinyl norbornene, norbornadiene, and the like.

20   The catalysts of this invention can be utilized in a variety of different polymerization processes. They can be utilized in a liquid phase polymerization process (slurry, solution, suspension, bulk phase, or a combination of these), in a

high pressure fluid phase, or in a gas phase polymerization process. The processes

can be used in series or as individual single processes. The pressure in the

polymerization reaction zones can range from about 15 psia to about 50,000 psia

and the temperature can range from about   -78°C to about 300°C.

5

EXAMPLE 1

Synthesis of Bis(2-pyridinoxy)titanium Dichloride

To a solution of 0.02 moles of 2-hydroxy pyridine and 0.02 moles of

triethylamine in 50 mL of THF, a solution of 0.01 moles of titanium tetrachloride was

added dropwise at 0°C and stirred overnight at room temperature. After filtration,

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the THF solution was evaporated and the product was extracted from the residue.

The product has the formula:

I.
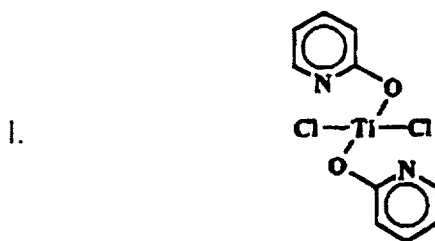
EXAMPLE 2

Preparation of (Cyclopentadienyl)
(2-Pyridinoxy) Titanium Dichloride

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To a solution of 0.002 moles of cyclopentadienyl titanium trichloride in 50 mL

of ether a solution of 2-hydroxy pyridine (0.002 moles) and triethylamine (0.002

moles) in 50 mL of ether was added at 0°C and stirred overnight. The product was

recovered from the ether filtrate. The product has the formula:
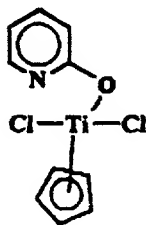
EXAMPLE 3

General Procedure For Preparation
of Quinolinoxy Transition Metal Catalysts

Toluene slurries of lithium salts of various 8-quinolinol derivatives (prepared

using butyl lithium) were combined with the corresponding titanium or zirconium

compound (titanium tetrachloride, zirconium tetrachloride, cyclopentadienyl titanium

trichloride, or cyclopentadienyl zirconium trichloride) at -78°C and stirred overnight at

room temperature. The complexes were recovered from the reaction mixture by

extraction with toluene or methylene chloride. To prepare 8-quinolinoxy titanium

trichloride (III)
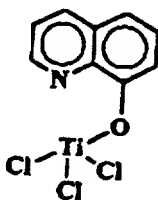
a slurry of 0.01 moles of the lithium salt of 8-hydroxyquinoline in 30 ml of toluene

(prepared from 1.45 g (0.01 moles) of quinolinol and MeLi) was added at -78°C to a

solution of 1.9 g (0.01 moles) of $TiCl_4$ in 20 ml of toluene and stirred overnight at

room temperature. The precipitate was separated, washed with toluene, and

5   extracted with 100 ml of CH_2Cl_2. After the methylene chloride had been removed, a

brown microcrystalline solid (0.7 g) was isolated.

Similarly, 8-(2-methyl-5,7-dichloroquinolin)oxytitanium trichloride (IV) (2.3 g)


IV
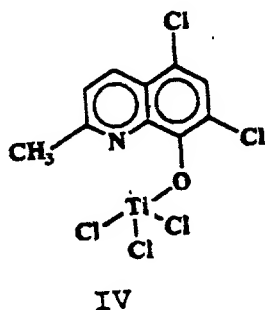
was prepared starting with a lithium salt made from 2.28 g (0.01 moles) of 5,7-

dichloro-2-methyl-8-quinolinol.

10   A similar procedure was used to prepare 1.0 g of the comparative complex

bis[8-(2-methyl-5,7-dichloroquinolin)oxy]zirconiumdichloride (V)
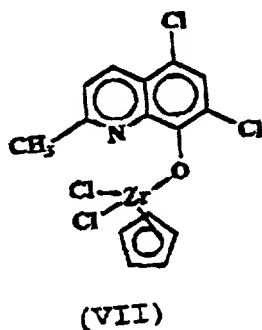

(V)

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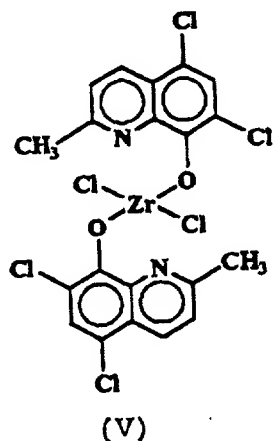
from 2.28 g (0.01 moles) of 5,7-dichloro-2-methyl-8-quinolinol and 1.165 g (0.005 moles) of zirconium tetrachloride.

To prepare (cyclopentadienyl)-(8-quinolinoxy)zirconium dichloride (VI)

(VI)
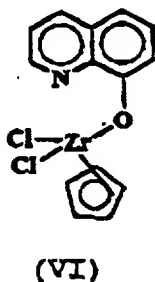
and (cyclopentadienyl)-[8-(2-methyl-5,7-dichloroquinolin)oxy]zirconium dichloride (VII)

(VII)

lithium salts made from 1.45 g (0.01 moles) of 8-quinolinol or 1.15 g (0.005 moles) of 5,7-dichloro-2-methyl-8-quinolinol, respectively, were reacted with equimolar amounts of cyclopentadienyl zirconium trichloride in toluene at -78°C. After stirring overnight and filtering, the products (0.62 g of VI and 1.7 g of VII) were isolated from

10   the toluene solution.

EXAMPLE 4

Polymerizations

All polymerizations in this study were conducted in a 1.7 L reactor. Prior to conducting a polymerization, the reactor was "baked-out" by heating to 130°C and holding at that temperature for 30 minutes under a nitrogen purge. Ethylene, hydrogen, hexene, butene, and nitrogen were treated by passage through columns containing 13X molecular sieves. For a typical polymerization, the reactor was charged with 0.850 L of hexane or toluene and, using a syringe, the required volume of diluted PMAO (AKZO). The desired amount of hydrogen was added to the reactor by monitoring the pressure drop (ΔP) from a 1 L stainless steel vessel pressurized with hydrogen. A toluene solution of catalyst was added to the reactor by nitrogen over pressure. The reactor was maintained at isothermal conditions throughout the run. Ethylene was admitted to the reactor and controlled at 150 psi with feed on demand via a pressure regulator. After the reactor temperature and pressure stabilized, the catalyst slurry was charged into the reactor and polymerization initiated. Ethylene flow was monitored via a Brooks mass flow meter.

Polymerization was terminated by venting the reactor and the polymer recovered by filtration. The polymer was stabilized by the addition of about 1000 ppm of butylated hydroxytoluene/hexane (BHT) and further devolatilized 2 hours at 80°C in a vacuum oven. Melt flow properties of the polymer were determined in accordance with ASTM D-1238. Polymer densities were measured on compression molded samples in a density gradient column in accordance with ASTM D-1505 85. The following table gives the reaction conditions.

Run	Catalyst	Temp. (°C)	Co-Monomer	Co-Monomer (grams)	Catalyst (mmoles)	Molar Ratio Al/M	H2, ΔP	Reaction Time (Min)
1	I	80	None	0	9.5E-3	1897	0	15
2	I	80	None	0	4.7E-3	3795	0	15
3	I	80	None	0	4.7E-3	1897	20	15
4	I	80	None	0	4.7E-3	1897	50	10
5	I	80	Butene	20	4.7E-3	1897	20	15
6	II	80	None	0	9.0E-3	1001	0	60
7	III	80	Butene	10	8.4E-3	1074	10	30
8	III	80	None	10	8.4E-3	1074	10	30
9	IV	80	Butene	0	6.6E-3	1324	0	30
10	IV	80	Butene	10	6.6E-3	1324	10	30
11*	V	80	Butene	10	1.14E-2	1175	0	10
12*	V	80	Butene	10	4.06E-3	1645	0	10
13*	V	80	Butene	10	8.12E-3	1645	0	10
14	VI	80	Butene	10	6.74E-3	991	0	15
15	VI	80	Butene	10	1.35E-2	991	0	15
16	VI	80	Butene	10	1.35E-2	1288	5	15
17	VI	80	Butene	10	1.89E-2	1132	15	15
18	VI	110	Butene	10	1.89E-2	1132	0	15
19	VII	80	Butene	10	1.10E-2	1212	0	15
20	VII	80	Butene	10	1.10E-2	1212	5	15
21	VII	110	Butene	10	1.54E-2	1126	15	15
22	VII	80	Butene	10	1.54E-2	1126	0	15
23	VII	80	Butene	10	1.54E-2	2078	0	15

In the table, "Al/M" is ratio of moles of aluminum in PMAO to moles of metal (titanium or zirconium) in the catalyst.

*Comparative Example

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The following table gives the result of the polymerizations.

Run	Catalyst Productivity (kg/gM/h)	MI2	MI20	MFR	Density	Mw/Mn
1	179.0	<0.01	<0.01	-		
2	153.2	<0.01	<0.01	-		
3	165.5	<0.01	1.8	-		
4	133.1	<0.01	2.47	-		
5	272.9	<0.01	0.964	-		
6	62.9	<0.01	<0.01	-		
7	99.2	0.90	16.9	18.9	0.9513	2.51
8	167.9	0.41	4.2	10.2		3.67
9	103.2	<0.01	-	-		
10	24.8	<0.01	-	-		
11*	low	-	-	-		
12*	none	-	-	-		
13*	none	-	-	-		
14	none	-	-	-		
15	98.1	<0.01	1.15	-		
16	177.7	0.93	21.4	23.1		
17	137.6	1.31	34.5	26.3		
18	159.0	0.81	16.1	19.8		
19	119.8	<0.01	.83	-		
20	198.7	0.46	11.4	24.7		
21	157.8	0.63	17.8	28.2		
22	160.1	0.06	12.8	-		
23	112.1	0.06	1.84	29.7		

In the table, kg/gm/h is kilograms polymer produced per gram of catalyst per

hour. The melt index of the polymer was measured according to ASTM D-1238,

Condition E and Condition F. MI2 is the melt index measured with a 2.16 kg weight (Condition E). MI20 is the melt index measured with a 21.6 kg weight (Condition F). MFR is the ratio of MI20 to MI2. The polymer density was measured according to ASTM D-1505. The molecular weight distribution of the polymer was measured

5   using a Waters 150C gel permeation chromatograph at 135°C with 1,2,4-dichlorobenzene as the solvent. Both weight average molecular weight (Mw) and the ratio of Mw to Mn (number average molecular weight) are used to characterize the molecular weight distribution.

The catalysts of this invention gave good productivities and high molecular

10   weight polymers, as evidenced by very low MI values, and Catalysts VI and VII did so even at higher temperatures (110°C).

EXAMPLE 5

Synthesis of Bis (2-pyridinoxy) Platinum Dichloride

To a solution of 0.02 moles of 2-hydroxypyridine and 0.02 moles of

15   triethylamine in 50 mL of THF, a solution of 0.01 moles of platinum tetrachloride is added dropwise at 0°C. The solution is then stirred overnight at room temperature. After filtration, the THF solution is evaporated and the product is extracted from the residue. Polymers may be produced using the catalyst by following the procedure of Example 4.

EXAMPLE 6

Synthesis of (2-Pyridinoxy) (Cyclopentadienyl) Vanadium Dichloride

To a solution of 0.002 moles of cyclopentadienyl vanadium trichloride in 50 mL of ether a solution of 2-hydroxy pyridine (0.002 moles) and triethylamine (0.002 moles) in 50 mL of ether is added at 0°C. The solution is stirred overnight. The product is recovered from the ether filtrate. An α-olefin polymer may be produced using the catalyst in accordance with the procedure of Example 4.

EXAMPLE 7

Synthesis of (8-Quinolinoxy) (Cyclopentadienyl) Niobium Trichloride

A solution of 0.01 moles of the lithium salt of 8-hydroxyquinoline in 30 mL of tetrahydrofuran (prepared as described in Example 3) is added dropwise to a solution of 0.01 moles of cyclopentadienyl niobium tetrachloride in 50 mL of tetrahydrofuran at -78°C. After warming to room temperature and stirring overnight, the suspension is filtered and the solvent evaporated under vacuum. The product is recovered by extraction with toluene and then isolated by evaporating the toluene. Polymers may be produced using this catalyst by following the procedure of Example 4.
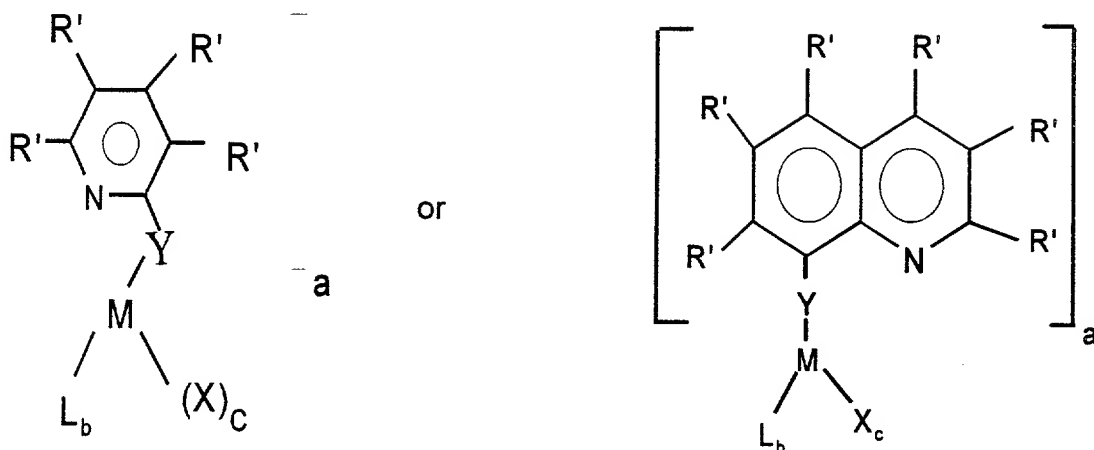
EXAMPLE 8

Synthesis of (8-Quinolinoxy) Chromium Dichloride

A solution of 0.01 moles of the lithium salt of 8-hydroxyquinoline (prepared as described in Example 3) in 50 mL of tetrahydrofuran is added dropwise to a solution of 0.01 moles of chromium trichloride in 50 mL of tetrahydrofuran at -78°C. After

warming to room temperature and stirring overnight, the suspension is filtered and the solvent evaporated under vacuum. The product is recovered from the solids by extraction with toluene and then isolated by evaporating the toluene. Polymers may be produced using this catalyst by following the procedure of Example 4.

5

EXAMPLE 9

Synthesis of bis (2-Pyridinoxy) Tungsten Tetrachloride

A solution of 0.01 moles of tungsten hexachloride in 20 mL tetrahydrofuran (THF) is added to a solution of 0.02 moles of 2-hydroxypyridine and 0.02 moles of

10 triethylamine in 50 mL THF at 0°C. The mixture is stirred while warming to room temperature, then stirred overnight. The mixture is then filtered and the THF evaporated under vacuum. The product is extracted from the residue with toluene and then recovered by evaporating the toluene. A polymer may be prepared by using the catalyst in accordance with the procedure described in Example 4.
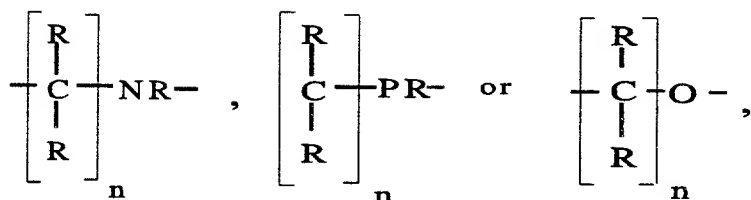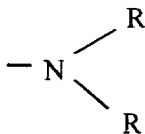
WE CLAIM:

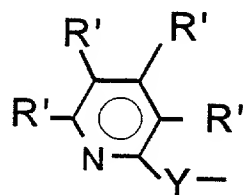1.   1.   A catalyst having the general formula

2   or
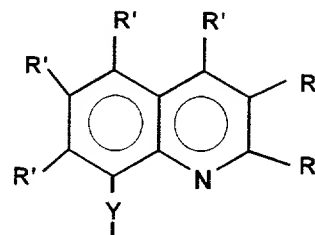
3   where Y is O, S, NR, PR,

$$\left[\begin{array}{c} R \\ | \\ C \\ | \\ R \end{array}\right]_n \!\!-\!\! NR- \;,\; \left[\begin{array}{c} R \\ | \\ C \\ | \\ R \end{array}\right]_n \!\!-\!\! PR- \; \text{or} \; \left[\begin{array}{c} R \\ | \\ C \\ | \\ R \end{array}\right]_n \!\!-\!\! O- \;,$$

4   each R is independently selected from hydrogen or C_1 to C_6 alkyl or C_6 to C_{14} aryl,

5   each R' is independently selected from R, C_1 to C_6 alkoxy, C_7 to C_{20} alkaryl, C_7 to C_{20}

6   aralkyl, halogen, or CF_3, M is a Group 3 to 10 metal, each X is independently

7   selected from halogen, C_1 to C_6 alkyl, C_6 to C_{14} aryl, C_7 to C_{20} alkaryl, C_7 to C_{20}

8   aralkyl, C_1 to C_6 alkoxy, or   ,

$$-N\!\!\begin{array}{c} \diagup R \\ \diagdown R \end{array}$$

9   L is X, cyclopentadienyl, C_1 to C_6 alkyl substituted cyclopentadienyl, indenyl,

10   fluorenyl, or

11   or

12   "n" is 1 to 4;

13   "a" is 1 to 3;

14   "b" is 0 to 2;

15    $a + b \leq 3$;

16   "c" is 1 to 6; and

17    $a + b + c$ equals the oxidation state of M.

1   2.   A catalyst according to Claim 1, wherein $a + b \leq 2$ when the oxidation state of

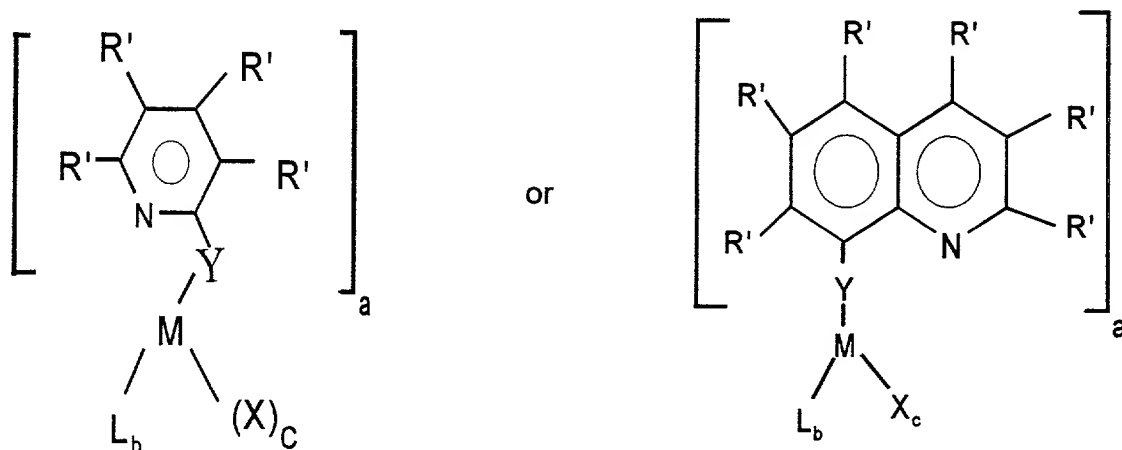2   M is 4 or less and $a + b \leq 3$ when the oxidation state of M is greater than 4.

1   3.   A catalyst according to Claim 2, wherein $a + b \leq 2$ when the oxidation state of

2   M is greater than 4.

1   4.   A catalyst according to Claim 1, wherein Y is oxygen.
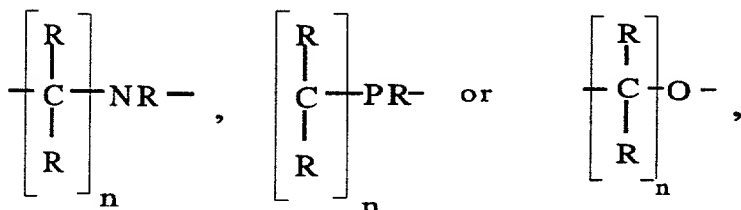
2   5.   A catalyst according to Claim 1, wherein X is halogen.

3   6.   A catalyst according to Claim 5, wherein X is chlorine.

1   7.   A catalyst according to Claim 1, wherein M is a Group 3 to 7 metal.

1   8.   A catalyst according to Claim 7, wherein M is a Group 4, 5 or 6 metal.

1   9.   A catalyst according to Claim 8, wherein Y is oxygen.

           10.   A catalyst according to Claim 8, wherein M is titanium, zirconium or hafnium.

           11.   A catalyst according to Claim 10, wherein M is titanium or zirconium.

           12.   A catalyst according to Claim 11, wherein Y is oxygen.

           13.   A catalyst according to Claim 11, wherein X is halogen.

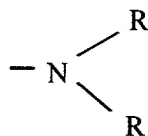1   14.   A catalyst according to Claim 12, wherein X is chlorine.

15. A method of making a poly-α-olefin comprising polymerizing an α-olefin

monomer using a catalyst that has the general formula

or

where Y is O, S, NR,

$$\left[\begin{array}{c} R \\ | \\ C \\ | \\ R \end{array}\right]_n NR- \ , \quad \left[\begin{array}{c} R \\ | \\ C \\ | \\ R \end{array}\right]_n PR- \quad or \quad \left[\begin{array}{c} R \\ | \\ C \\ | \\ R \end{array}\right]_n O- \ ,$$

each R is independently selected from hydrogen, C_1 to C_6 alkyl, C_6 to C_{14} aryl, each

R' is independently selected from R, C_1 to C_6 alkoxy, C_7 to C_{20} alkaryl, C_7 to C_{20}

aralkyl, halogen, or CF_3, M is a Group 3 to 10 metal, each X is independently

selected from halogen, C_1 to C_6 alkyl, C_6 to C_{14} aryl, C_7 to C_{20} alkaryl,

C_7 to C_{20} aralkyl, C_1 to C_6 alkoxy, or

$$-N \overset{\displaystyle R}{\underset{\displaystyle R}{\diagup}} ,$$

L is X, cyclopentadienyl, C_1 to C_6 alkyl substituted cyclopentadienyl, indenyl,

11   fluorenyl, or
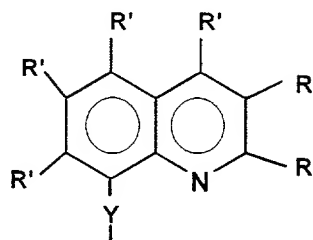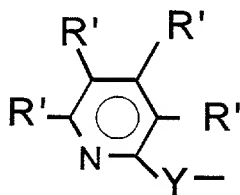
12   "n" is 1 to 4;

13   "a" is 1 to 3;

14   "b" is 0 to 2;
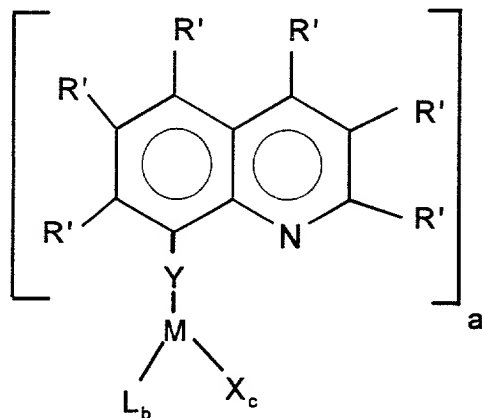
15        $a + b \leq 3$;

16   "c" is 1 to 6; and

17        $a + b + c$ equals the oxidation state of M.

1   16.   A method according to Claim 15, wherein said catalyst has the general

2   formula

1   17.   A catalyst according to Claim 16, wherein $a + b \leq 2$ when the oxidation state

2   of M is 4 or less and $a + b \leq 3$ when the oxidation state of M is greater than 4.
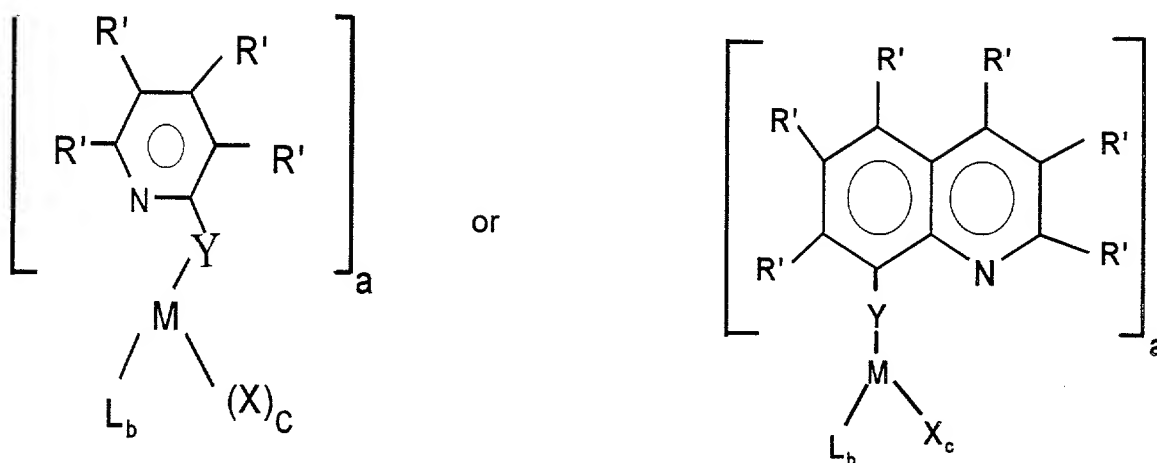

18.   A catalyst according to Claim 17, wherein $a + b \leq 2$ when the oxidation state

of M is greater than 4.

19.   A method according to Claim 17, wherein Y is oxygen.
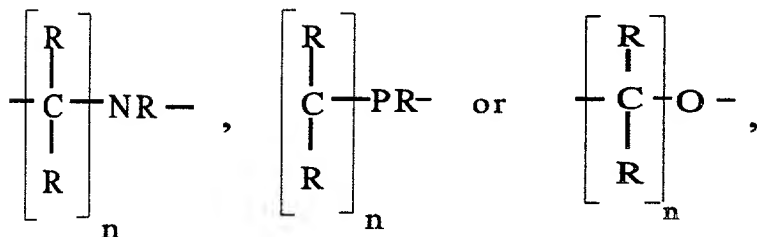

20.   A method according to Claim 16, wherein M is a Group 4 to 6 metal.

Abstract of the Disclosure

Disclosed is a novel bidentate pyridine transition metal catalyst having the general formula
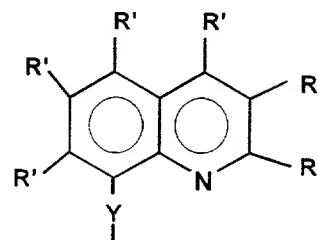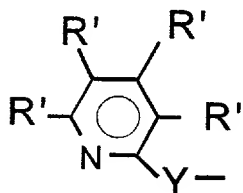

or

where Y is O, S, NR,

each R is independently selected from hydrogen or C_1 to C_6 alkyl, or C_6 to C_{14} aryl, each R' is independently selected from R, C_1 to C_6 alkoxy, C_6 to C_{14} aryl, C_7 to C_{20} alkaryl, C_7 to C_{20} aralkyl, halogen, or CF_3, M is a Group 3 to 10 metal, each X is independently selected from halogen, C_1 to C_6 alkyl, C_6 to C_{14} aryl, C_7 to C_{20} alkaryl,

C_7 to C_{20} aralkyl, C_1 to C_6 alkoxy, or

$$-N\begin{smallmatrix}R\\ \\R\end{smallmatrix} \quad ,$$
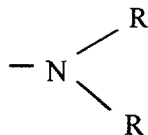
L is X, cyclopentadienyl, C_1 to C_6 alkyl substituted cyclopentadienyl, indenyl, fluorenyl, or

"n" is 1 to 4;

"a" is 1 to 3;

"b" is 0 to 2;

$a + b \leq 3$;

"c" is 1 to 6; and

$a + b + c$ equals the oxidation state of M.